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The role of deep donor–deep acceptor complexes in CIS-related compounds

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Abstract

Deep PL emission bands are observed in several samples of $CuGaSe_2$, $CuIn_{0.5}Ga_{0.5}Se_2$ and $CuInS_2$. In all these materials these bands have a closely similar structure. The D1 and D2 bands centered at $h\nu = 1.148$ and 1.042 eV in $CuGaSe_2$, at $h\nu = 0.948$ and 0.857 eV in $CuIn_{0.5}Ga_{0.5}Se_2$, and at $h\nu$(= 0.954 eV and 0.864 eV in $CuInS_2$, respectively, are concluded to result from a donor–acceptor pair (DAP) recombination, such that the donor atom of the DAP occupies an interstitial position within the chalcopyrite lattice and the acceptor atom resides at a cation site (either In or Ga) next to it. The probable donor defect is identified as an interstitial Cu atom and the associated acceptor defect as a cation vacancy, i.e. either V_{In} or V_{Ga}. On the basis of the simple Coulombic interaction $Z_A Z_D e^2/(\varepsilon r)$ between the components of the DAP, additional deep bands D3, D4, D5,...,are predicted. In the present work we find these additional emissions experimentally in $CuInS_2$ and $CuIn_{0.5}Ga_{0.5}Se_2$, but not in our $CuGaSe_2$ samples. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recent years have indicated that in order to reach a profound understanding of the defect structure of ternary chalcopyrite compounds it is necessary to study experimentally more thoroughly the deep defects. Although these deep defects have little direct influence on the electrical properties of the ternary compounds they can be quite effective recombination centers. Moreover, deep defects easily form complexes with shallow defects and thus indirectly affect electrical properties.

Photoluminescence (PL) spectroscopy is a very general and widely used method to analyze the defect structure of semiconductors. Unfortunately, most of the PL studies of chalcopyrite semiconductors, so far, have been focused on relatively shallow PL bands having a peak position near the bandgap energy. Much less is known experimentally about possible deep PL bands, with emission energies $h\nu < E_g - 0.4$ eV and, as a result of this, about the related deep electronic gap levels in these compounds.

As it was concluded in Ref. [1], some of these deep PL bands found in $CuInS_2$ and $CuGaSe_2$ can be explained as an electron–hole recombination within donor–acceptor (DA) pairs involving deep donor and deep acceptor levels. In the present study we focused our attention on further aspects of these deep donor–deep acceptor centers in various ternary compounds.

2. Experimental

$CuGaSe_2$ and $CuInS_2$ single crystals were grown in closed ampoules from a stoichiometric mixture of the elements (6N purity) by chemical vapor transport at temperatures between 800°C and 750°C using iodine (about 3 mg/cm^3) as the transport agent. Some of the crystals were also grown by the vertical Bridgman technique. In addition we also used some $CuIn_{0.5}Ga_{0.5}Se_2$ and $CuInS_2$ polycrystalline samples which were evacuated and sealed into quartz ampoules and heat treated in muffle furnace. The objects were heated to 500°C and held for 1 h. Then a slow cooling program started: at a cooling rate of 3°C/h to 300°C, following at a rate of 2°C/h to 150°C and then cooling with the whole furnace to room temperature. Further details of the crystal growth and characterization can be found in [1].

A Kr-ion laser at a wavelength of 568.2 nm and a He–Cd laser at a wavelength of 441 nm were used as the excitation

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source for steady-state PL measurements at temperatures ranging from 2 to 300 K. The laser beam was focused onto the sample with a spot diameter of about 100 μm and the luminescent light was analyzed with a 1 m grating monochromator and detected by either a liquid nitrogen cooled germanium detector, PbS detector, InGaAs detector or a photomultiplier tube with S1-characteristics. All samples were etched prior to measurement in a solution of bromine in methanol in order to ensure good and comparable surface properties.

3. Deep donor–deep acceptor pairs

It is known that the emission energy from a DA pair separated by a distance r is obtained from [2]

$$E(r) = E_g - \left(E_A^0 + E_D^0\right) + \frac{Z_D Z_A e^2}{\varepsilon r} - \Gamma(r) \quad (1)$$

Here E_g is the band gap energy, E_A^0 and E_D^0 the acceptor and donor ionization energies, ε is the dielectric constant, Z_D, Z_A are the charges of donor and acceptor, respectively, and $\Gamma(r)$ is an additional term which includes interactions relevant at very short distances only. There are different opinions as regards the details of this last term, but the main result is that in the case of distant pairs it gives only minor, second-order corrections to Eq. (1). However, as was shown by Williams [2], the magnitude of $\Gamma(r)$ may exceed 25 meV or even more in case of very short donor–acceptor distances. Therefore, the theoretically calculated Coulombic energy usually tends to be higher than the energy found from experiment. An open question is the appropriate value for the dielectric constant ε in case of very close pairs. In compound semiconductors it is obvious, that ε must be a combination of both optical and static dielectric constants ($\varepsilon_\infty < \varepsilon < \varepsilon_0$), but the exact numerical value for it is hard to predict. Therefore Eq. (1) must be considered as a very rough method to calculate the transition energy of close DA pairs.

It is also known that the electron (hole) wave function in the deep donor (acceptor) level must be highly localized. Because of this, for more distant pairs, there is practically no overlap of the initial and final state wave functions and, as a result of this, no observable recombination emission. It seems to be a reasonable assumption that both the donors and the acceptors can occupy only few energetically favorable positions within the chalcopyrite crystal. Then it is possible to calculate, using Eq. (1) and by assuming that $\Gamma(r_1) \approx \Gamma(r_2)$, the approximate energy difference ΔE between the DA pair emissions for the shortest and the next-shortest DA separation, r_1 and r_2, respectively

$$\Delta E = \frac{Z_D Z_A e^2}{\varepsilon}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \quad (2)$$

A similar calculation can be continued with more distant pairs with DA separations r_3, r_4, r_5 and so on. By resorting to the energy difference ΔE instead of the absolute energies E of Eq. (1) we reduce the disturbing role of the $\Gamma(r)$ term in our calculations.

In [1] we calculated, using Eq. (2), all possible energy separations ΔE for donor–acceptor pairs and compared them with the experimentally measured deep PL band positions in $CuInS_2$ and $CuGaSe_2$. These calculations showed that the observed deep PL bands must be related to such DA pairs where one of the components (donor or acceptor) is located at an interstitial position. Note that there are two types of interstitial positions in the chalcopyrite lattice (i_1 and i_2). Taking the unit cell corners to be defined by the cations (i.e. at each corner either Cu or Ga), these interstitial positions have the coordinates (1/2; 1/2; 1/4) and (3/4; 3/4; 3/8), respectively. It is important to realize that these two interstitials have a different surrounding. The first one (i_1) is surrounded by six cation sites and four anion sites, and the second one (i_2) by four cation sites and six anion sites, respectively. Assuming one component of the DA pair is situated at the interstitial position (either i_1 or i_2) and the other component takes a position of Cu, Ga or In, it is possible to calculate spatial distances and energy separations for nearest DA pairs. The first 6 distances are given in Table 1.

The distances in Table 1 are given for an ideal chalcopyrite lattice. It is known that in ternary chalcopyrite compounds the crystal lattice is affected by the tetragonal distortion and therefore the group-VI anions (Se and S) are slightly displaced from their ideal positions. This fact makes it difficult to claim precise and correct calculated values of ΔE, but, at least, we can obtain a first order approximation.

4. Results and discussion

In as-grown $CuInS_2$ crystals only D1 and D2 PL bands were detected. Their peak positions were 0.954 and 0.864 eV, respectively, see Fig. 1. After low-temperature annealing at 400–500°C in some polycrystalline samples we detected additional deep PL bands at about 0.6 eV, see Fig. 1. Using lattice parameters $a = 0.5523$ nm and $c = 1.1123$ nm [3], distances from Table 1 and Eq. (2) it

Table 1
The six shortest donor-to-acceptor separations r in the chalcopyrite lattice with lattice parameters a and c, used for the ΔE calculation in conjunction with Eq. (2). One component of the DA pair is assumed to occupy an interstitial position (i_1 or i_2), the other is assumed to be at a cation lattice site

Pair	Separation r	Corresponding PL band	Corresponding interstitial position
1	$r = \sqrt{a^2/8 + c^2/64}$	D1	i_2
2	$r = a/2$	D2	i_1
3	$r = \sqrt{a^2/8 + 9c^2/64}$	D3	i_2
4	$r = \sqrt{10a^2/16 + c^2/64}$	D4	i_2
5	$r = \sqrt{a^2/2 + c^2/16}$	D5	i_1
6	$r = (\sqrt{5/4})a$	D6	i_1

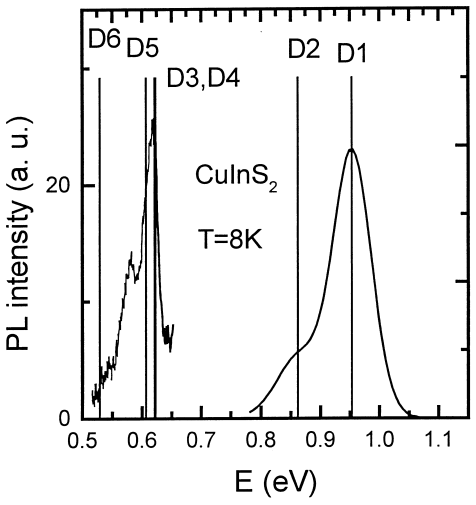

Fig. 1. The measured deep PL bands in $CuInS_2$ single crystal (D1–D2) and in polycrystalline sample (D3–D6). The vertical lines show the positions of the bands calculated by Eq. (2). The D1, D2 and the D3–D6 PL bands, respectively, were measured using different detectors and gratings.

is possible to calculate the energetic distance of corresponding PL bands from the D1 PL band. The position of the D1 PL band was taken from the experiment. Comparing the experimentally measured peak positions with calculated ones we can find an optimal value for the dielectrical constant ε. In the case of $CuInS_2$ $\varepsilon = 8.7$. This value lies indeed between the optical and static values, see Table 2. It is worth noting that $Z_D = Z_A = 1$ in our calculations.

The intensity of D3–D6 PL bands in polycrystalline $CuInS_2$ was relatively high and therefore we were able to measure the temperature quenching of the integral PL emission in this region, see Fig. 2. In order to find an activation energy of this quenching process we used the equation [4]

$$I(T) = \frac{I_0}{1 + \varphi_1 T^{3/2} + \varphi_2 T^{3/2}\exp(-E_T/kT)} \quad (3)$$

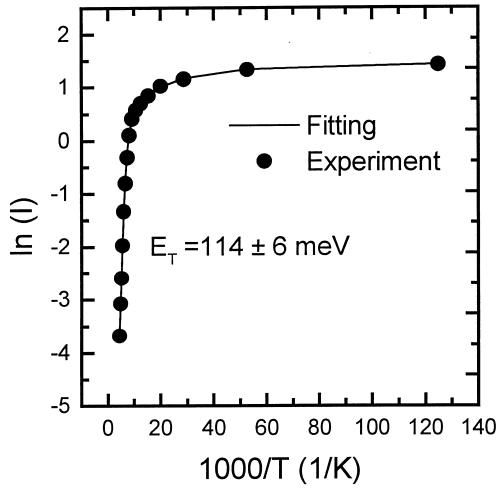

Fig. 2. Temperature dependence of the integrated intensity of the D3–D6 PL bands in $CuInS_2$. The continuous curve shows the result of parameter fitting to Eq. (3) with parameter values as given in the text.

Table 2
Dielectrical constants ε conforming to the present experimental work together with the ε_0 and ε_∞ values found in the literature

	ε (present work)	ε_0	ε_∞	Reference
$CuInS_2$	8.7	10.2	6.3–7.8	[11,12]
$CuGaSe_2$	7.8	9.6	6.7	[13]
$CuIn_{0.5}Ga_{0.5}Se_2$	8.8	9.6–10.9	6.7–7.6	[13]

where φ_1, φ_2, I_0 and E_T are the fitting parameters. As was shown in [4] this equation includes the temperature dependence of the capture cross-sections of both the donor and the acceptor defects and therefore it should give a more correct fit especially at the low-temperature region. The best fit was achieved with parameters $\varphi_1 = 1.63 \times 10^{-3}$, $\varphi_2 = 13.91$, $I_0 = 4.27$ and $E_T = 114 \pm 6$ meV, see Fig. 2. Our previous results have shown that the thermal quenching energies for D1 and D2 PL bands in $CuInS_2$ were 39 ± 3 and 64 ± 7 meV respectively. It is known that the acceptor level is moving closer to the valence band when paired with a donor defect. Assuming that the quenching is mainly caused by ionization of the acceptor level we can predict that the isolated acceptor defect involved in this DA pair must have a level somewhat deeper than the obtained E_T value for D3–D6 bands, i.e. $E_A > E_T = 114$ meV.

In $CuGaSe_2$ only D1 and D2 PL bands were detected at 1.148 and 1.042 eV, respectively, see Fig. 3. Lattice parameters $a = 0.5607$ nm and $c = 1.1054$ nm [5] were used in calculations. The best fit was found with $\varepsilon = 7.8$ and this value seems to be quite reasonable. We were not able to detect deeper PL bands. One reason for this may be the high temperature of preparation of these crystals. It is obvious that at higher temperatures DA pairs with larger distances are hard to form because the thermal energy exceeds the Coulombic energy.

The $CuIn_{0.5}Ga_{0.5}Se_2$ samples were synthesized at relatively low temperatures and this is maybe a main reason

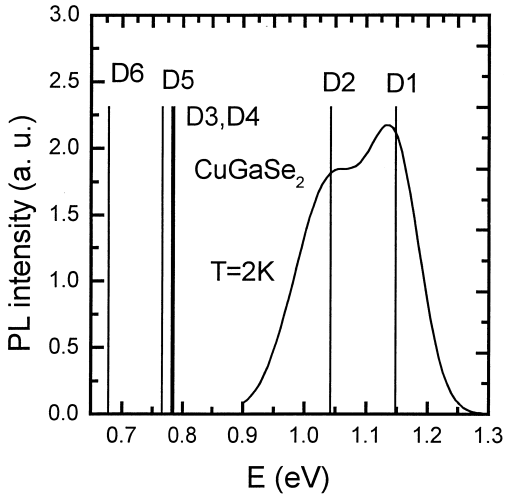

Fig. 3. The measured deep PL bands in single crystal $CuGaSe_2$. The vertical lines show the positions of the bands calculated by Eq. (2).

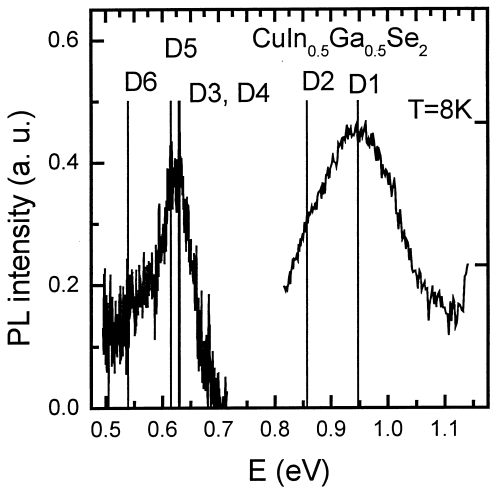

Fig. 4. The measured deep PL bands in polycrystalline $CuIn_{0.5}Ga_{0.5}Se_2$. Calculated positions of PL bands are given as a vertical lines. The D1, D2 and the D3–D6 PL bands, respectively, were measured using different detectors and gratings.

that in this material we were able to detect additional, deeper PL bands, see Fig. 4. In $CuIn_{0.5}Ga_{0.5}Se_2$ the D1 and D2 PL bands were detected at 0.948 and 0.857 eV respectively. The optimal fitting value for the dielectric constant was $\varepsilon = 8.8$. Lattice parameters $a = 0.56905$ nm and $c = 1.12995$ nm [6] were used. Unfortunately the intensity of D3–D6 PL bands was very weak and we could not measure the temperature dependence.

In [1] it was shown that annealing in the presence of Cu enhances the intensity of deep PL bands in $CuInS_2$ and $CuGaSe_2$. Therefore it is most probable that we are dealing with a Cu_i, a deep donor defect. It is known that an interstitial copper ion is highly mobile in most ternaries. Therefore all kinds of annealing (*except* the Cu-annealing) should tend to reduce the concentration of Cu_i (and the intensity of the deep PL bands, also) through the simple reaction $V_{Cu} + Cu_i \rightarrow Cu_{Cu}$. However, the deep donor levels with $E_D > 0.4$ eV are not so often observed in $CuInSe_2$ and related ternaries. At the same time the most recent theoretical calculations [7,8] have shown that Cu_i is not such a deep donor in the ternaries and, in fact, apparently does not exceed the value $E_D = 0.21$ eV in $CuGaSe_2$. Therefore it is obvious that the $\Gamma(r)$ term in Eq. (1) has quite a large value.

The most probable candidate for the acceptor defect of this DA pair seems to be V_{In} (in case of $CuInS_2$) or V_{Ga} ($CuGaSe_2$). According to the latest calculations of defect structure in the CIS related ternary compounds these vacancies are responsible for the A3 level with $E_{A3} \approx 150$ meV [8]. Moreover, the V_{Ga} level seems to be slightly deeper acceptor than the V_{In} level [7,9]. Accordingly, the thermal quenching energy for the D1 PL band in $CuGaSe_2$ is also predicted slightly higher than in $CuInS_2$. Indeed, the measured activation energies in $CuInS_2$ and $CuGaSe_2$ were 39 and 55 meV [1] respectively. This fact confirms our model. It is interesting that the same kind of deep PL bands were also found in CdTe [10].

5. Conclusions

Closely similar D1 and D2 deep PL bands have been observed in several samples of $CuGaSe_2$, $CuIn_{0.5}Ga_{0.5}Se_2$ and $CuInS_2$. These deep bands seem to find a consistent explanation by assuming that they originate in a DAP recombination emission, such that the donor component of the DAP occupies an interstitial position (either i_1 or i_2) within the chalcopyrite lattice and the acceptor component resides at a cation site (either In or Ga) next to it. We conclude that the probable donor defect is an interstitial Cu atom and, further, suggest that the associated acceptor defect is a cation vacancy, i.e. either V_{In} or $V_{Ga.}$

The structural model presented here, in order to explain the observed D1 and D2 deep PL bands, predicts that in addition to the closest possible DA pairs, responsible for the D1 and D2 bands, the same DAP defects, but with a larger spatial separation than that for the nearest and the next nearest interstitial–cation site distance, should be present. We found that, apparently, the energetic distance between the experimentally observed D1 and D2 emission bands could be fairly precisely estimated by a simple Coulombic type interaction between a singly charged donor and a singly charged acceptor. Within this model, then, we were in a position to predict the energies at which these larger DAP separation recombination emissions D3, D4, D5,…,should occur. Accordingly, these emissions were searched for and also found in $CuInS_2$ and $CuIn_{0.5}Ga_{0.5}Se_2$. However, no trace of those larger separation DAP emissions were detected in $CuGaSe_2$, probably indicating that in our $CuGaSe_2$ samples virtually only the two closest separation DAPs were present.

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